

The Absence of Superconductivity in Single Phase CaFe_2As_2 under Hydrostatic Pressure

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Recent high-pressure studies found that superconductivity can be achieved under very low pressure in the parent iron arsenide compound CaFe_2As_2 , although details of the sharpness and temperature of transitions vary between liquid medium and gas medium measurements. To better understand this issue, we performed high-pressure susceptibility and transport studies on CaFe_2As_2 , using helium as the pressure medium. The signatures of the transitions to the low-temperature orthorhombic and collapsed tetragonal phase remained exceptionally sharp and no signature of bulk superconductivity was found under our hydrostatic conditions. Our results suggest that phase separation and superconductivity in CaFe_2As_2 are induced by non-hydrostatic conditions associated with the frozen liquid media.

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The recent discovery of superconductivity in doped iron arsenide compounds[1, 2, 3] and the later improvement of the superconducting transition temperature T_c in both the pnictide oxides such as ROFeAs (R111) [4, 5, 6, 7] and the ThCr_2Si_2 -structure compounds such as $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$ (R122) [3] have caused extensive experimental and theoretical studies in this new class of materials with layered FeAs planes. Similar to the high- T_c cuprates, the parent compounds exhibit structural transitions from a high-temperature tetragonal phase to a low-temperature orthorhombic phase, and the orthorhombic phase is usually antiferromagnetically (AF) ordered[8]. Upon doping, both the orthorhombic structure and the AF phase are suppressed and superconductivity is induced.

Several unique properties have been found in the iron arsenide superconductors. For example, these materials are semimetals and therefore metallic even without doping, in contrast to the cuprates. In BaFe_2As_2 , doping Co into the FeAs-plane also induces superconductivity [9], which differs from the suppression of superconductivity and formation of local moments by any doping into the cuprate CuO-planes. Superconductivity has been reported under hydrostatic pressure in the parent compounds CaFe_2As_2 [10, 11, 12], SrFe_2As_2 [13, 14, 15], and BaFe_2As_2 [14]. In particular, for CaFe_2As_2 , T_c as high as 10K has been found in a moderate 0.4GPa pressure [10, 11, 12], while for SrFe_2As_2 and BaFe_2As_2 , superconductivity is achieved at about 28K at $P=3.2$ GPa and 4.5 GPa respectively [14].

In CaFe_2As_2 in ambient pressure, a structural phase transition (from tetragonal to orthorhombic) is seen at $T_{S1} = 170$ K[16], accompanied by the appearance of magnetic order[17]; this transition is seen as a sharp upwards anomaly in resistivity. Hydrostatic pressure

causes a reduction of T_{S1} . The signature in resistivity becomes a broad upturn, rather than the sharp discontinuous change seen in ambient pressure[10, 12]. Above 0.5GPa, a collapsed tetragonal structure is identified below a separate structural transition temperature (T_{S2}) [10, 18]. The collapsed tetragonal phase has the same crystal symmetry as the high-temperature one, but with a $\sim 10\%$ reduction in the c-axis parameter and a 2% expansion of the in-plane lattice parameters [18]. The transition to the collapsed phase is also seen[19] in resistivity measurements, where a broad downward change in slope has been observed. The temperature T_{S2} increases with further increases in pressure[10, 18]. The transition of CaFe_2As_2 from the high temperature tetragonal phase to either of the low temperature phases seems very sensitive to different pressure conditions. Transport studies using a conventional clamp cell see wide transitions [10, 12], whereas neutron scattering using helium as the pressure medium suggests that the orthorhombic and collapsed tetragonal phases emerge sharply at low temperatures [18]. The maximum superconducting T_c is achieved at about 10K around an inferred phase boundary $P\approx 0.5$ GPa [10, 12] between the two low temperature structures. This near vertical boundary was explicitly detected in isothermal pressure sweeps[18, 20]. Recently Lee *et al.* postulated[12] the existence of a third phase in the region of the phase boundary and associated superconductivity with that border phase.

In order to clarify the phase diagram and the nature of the various phase transitions we have studied the high-pressure dc susceptibility and resistivity of CaFe_2As_2 using a helium gas pressure system. Compared with clamp pressure cells, helium has a low freezing point, which only increases to about 50 K at $P= 0.7$ GPa. CaFe_2As_2 single crystals were grown by the Sn-flux method [16], and

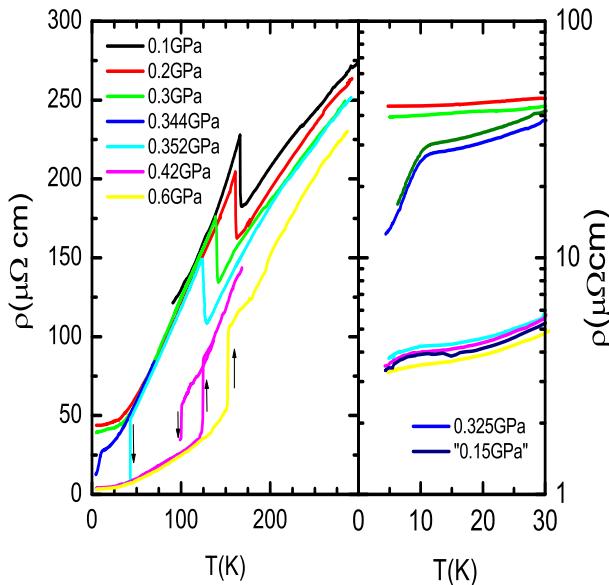


FIG. 1: (a) The resistivity of a CaFe_2As_2 single crystal at different pressures. For pressures above 0.35 GPa, the cooling or the warming up direction is indicated by an arrow next to the plots. (b) The low-temperature resistivity of the same CaFe_2As_2 crystal. The 0.15 GPa data is taken after decreasing pressure from 0.4 GPa to 0.15 GPa at $T=50$ K.

afterwards surface Sn was removed by etching with HCl. For the transport measurements, samples were loaded in a pressure cell with either a four-probe or a Van der Pauw configuration. The pressure cell was cooled in a helium storage dewar and the pressure was applied *in situ* by an external helium compressor. For the magnetization measurements using a Quantum Design MPMS, the sample was loaded in a separate cell which was connected to the same helium compressor. The maximum pressure was about 0.7 GPa for both pressure cells and we employed a cooling rate of about 1 K/min through the structural transitions.

Fig. 1(a) shows the resistivity of a CaFe_2As_2 single crystal under different pressures. All measurements were reproducible from sample to sample. At ambient pressure, the sample shows a sharp increase of resistivity at $T_{S1} \approx 170$ K, corresponding to a first order structural transition from the tetragonal phase to the orthorhombic/AF phase [16, 17]. The residual resistance ratio (RRR) of our sample is about 5-6, which is similar to the other reports of etched samples [10, 12, 16]. The resistivity decreases gradually with pressure at room temperature. As pressure increases to 0.344 GPa, T_{S1} decreases to 120 K, and a sharp first order phase transition is still clearly seen. This is very different from previous measurements in clamp cells where the resistivity changes

gradually with pressure and becomes smooth with temperature at high pressures [10, 12]. Above 0.4 GPa, the transition to the orthorhombic phase, with its sharp upwards anomaly in resistivity disappears completely.

For $P \geq 0.4$ GPa, a second phase transition occurs at about $T_{S2}=100$ K with a sudden drop of resistance as seen in Fig. 1(a), which is known to be from the high-temperature tetragonal to the low-temperature collapsed tetragonal structure[21]. T_{S2} increases with increasing pressure, in agreement with the neutron[18] and transport[10, 12] results. Our data show the following features of the second phase. i) *Low resistivity*. From the high-temperature tetragonal phase to the collapsed tetragonal phase, the resistivity drops by a factor of two at the transition for all pressures. As seen in Fig. 1(b), the residual resistivity of the collapsed phase is about $3.5 \mu\Omega\text{cm}$, which is about about one-tenth that of the low-pressure orthorhombic phase. As originally reported[10] the RRR is about 70, which barely changes with pressure once saturated. ii) *Sharp transitions*. At all pressures, the resistance drops steeply through the transition with a transition width less than 1 K. This is a striking difference from the liquid medium measurements[10, 12]. iii) *Large thermal hysteresis*. As shown in Fig. 1(a), the onset temperature of the structural transition changes by 20 K during the cooling and warming up process at $P=0.42$ GPa, which form a hysteresis loop. This is similar to hysteresis reported in ref.[10, 12]. iv) *Hysteresis with pressure*. The collapsed tetragonal phase also shows a strong hysteresis with pressure. As shown in Fig. 1(b), by decreasing the pressure from 0.4 GPa to 0.15 GPa at 50 K, the collapsed tetragonal phase is still trapped as indicated by the low resistivity value. The orthorhombic phase is only recovered below 0.1 GPa. This is consistent with scattering measurements taken in He cells[18, 20].

The phase boundary between the orthorhombic phase and the collapsed tetragonal phase is found at $P \approx 0.35$ GPa. We did fine tuning of the pressure in steps of 0.01 GPa close to 0.35 GPa, and saw a direct transition between the orthorhombic phase and the collapsed tetragonal phase upon cooling at 0.354 GPa. As shown in Fig. 1(a), the sample first goes to the orthorhombic phase with a sharp increase of resistivity at $T_{S1} \approx 110$ K. On further cooling, there is a direct transition from the orthorhombic to the collapsed tetragonal phase with a dramatic decrease of resistivity at $T_{S2} \approx 45$ K.

Our magnetization data are consistent with the transport results. In Fig. 2 (a), the zero-field cooled (ZFC) dc susceptibility of CaFe_2As_2 is shown for various pressures. At ambient pressure, a drop of susceptibility is clearly seen at the structural transition temperature $T_{S1} \approx 170$ K. The transition temperature drops to 125 K at $P \approx 0.3$ GPa. Further increase of pressure causes another sharp drop of susceptibility at $T \approx 140$ K with $P \approx 0.5$ GPa, and $T \approx 150$ K with $P \approx 0.6$ GPa, which is

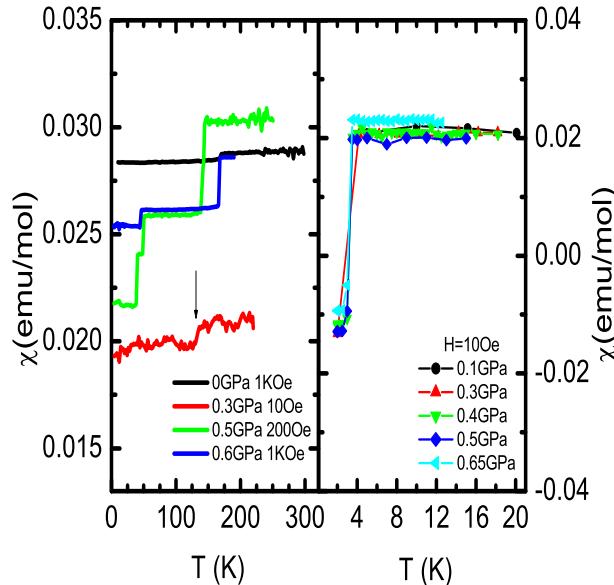


FIG. 2: (a) The zero-field-cooled dc susceptibility of CaFe₂As₂ single crystals under pressure measured in the MPMS. The magnetic field is aligned along the crystalline a (or b) axis. (b) The low-temperature dc susceptibility with an applied magnetic field of 10 Oe.

consistent with the structural transition T_{S2} seen in resistivity. Below T_{S2} , another drop of susceptibility is seen at $T \approx 50$ K for $P = 0.5$ – 0.6 GPa. However, this temperature corresponds to the helium solidification temperature at these pressures, which suggests that the collapsed tetragonal phase is very sensitive to even the small changes in the pressure environment when the helium freezes and does not represent an additional phase transition. The susceptibility below 20 K is shown in Fig. 2(b). For all pressures, we did not see any diamagnetism down to 4 K. Below 4 K, there is a diamagnetic signal at all pressures as shown in Fig. 2(b). We ascribe this diamagnetism to superconductivity of very small amounts of unetched tin flux, noting that the superconducting volume corresponds to only about 0.5% of the total sample volume.

In Fig. 3 we have constructed a (P, T) phase diagram from our transport and susceptibility measurements. The transition temperature measured during warm up is consistent for both techniques. For the higher pressure structural transition, the transition temperature first rises quickly with pressure from $P \approx 0.35$ GPa to 0.4 GPa, and then increases by about 20 K/kbar above 0.4 GPa; there is about 20 K of hysteresis in the T_{S2} transition.

Our results are quite different from the transport data using the clamp cells in a few aspects. First, we found a clear phase boundary at $P \approx 0.35$ GPa where the orthorhombic phase changes to the collapsed tetragonal

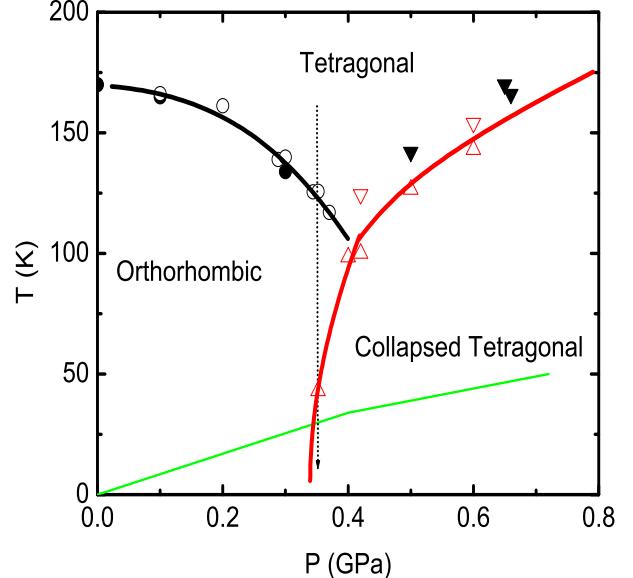


FIG. 3: The (pressure, temperature) phase diagram of CaFe₂As₂ constructed from the transport and susceptibility measurements. The solid circles and the solid inverted triangles correspond to T_{S1} and T_{S2} respectively measured by susceptibility during warm up after ZFC. The hollow circles and the hollow inverted triangles correspond to T_{S1} and T_{S2} respectively measured by transport during warm up. The hollow triangles correspond to T_{S2} measured by transport during cooling down. The dashed line shows two structural transitions at the pressure $P = 0.352$ GPa. The green line is the helium solidification temperature for reference.

phase with temperature or pressure abruptly. Second, the higher pressure structural transition is of the first order type, which is indicated by the narrow transition width and the hysteresis with pressure and temperature. Finally and most importantly, we did not see bulk superconductivity at any pressure up to 0.65 GPa. Careful examination of our transport data at $P \leq 0.344$ GPa in Fig. 1(b) shows a drop of resistivity at $T \leq 10$ K. Since superconductivity is reported at $T \approx 10$ K by previous transport studies above 0.3 GPa, the drop of resistivity in our case might be caused by some superconducting islands. However, any such superconducting regions should be very small since the resistivity is still quite high at 4.2 K and no signature is seen in susceptibility.

A major difference between the helium pressure cell and the liquid media pressure cells is that helium's solidification temperature is much lower and that even when frozen, helium cannot support much shear stress. As shown in Fig. 3, the helium solidification temperature increases to about 50 K at $P \approx 0.6$ GPa, and is much lower than both structural transition temperatures. At a temperature below the helium solidification temperature,

as shown in Fig. 2(a), a sharp drop of susceptibility is clearly seen. In contrast, the solidification temperature of other pressure mediums, for example FC-77, is usually much higher than 100 K at $P \approx 0.35$ GPa. Therefore it is likely that the pressure is non-hydrostatic through the structural transitions around the phase boundary $P \approx 0.35$ GPa.

In CaFe_2As_2 the lattice parameters change dramatically at the transition to the collapsed tetragonal phase[18] and so pressure homogeneity will be an issue if the sample is embedded in a solid pressure medium at the transition temperature. For example at $P \approx 0.4$ GPa, the structural transition causes a decrease of the c-axis lattice parameter by $\sim 10\%$ and an increase in the a-axis parameter by $\sim 2\%$. For the worst case, *i.e.*, assuming that the frozen pressure medium is unable to make plastic adjustment with the volume change of the sample, then the sample clearly must phase separate. Such a *constant volume* assumption upon cooling, rather than a constant pressure one, seems consistent with the μSR studies using naphthalene as the pressure medium, where a 50% volume fraction of the magnetic phase is seen at $P \approx 0.5$ GPa [22] as well as recent neutron results[20].

Non-hydrostatic conditions may cause the formation of domains with different properties (possibly including superconductivity). In a non-hydrostatic condition, large domain walls may be generated between highly phase-separated regions. Since the low-temperature orthorhombic and the tetragonal phase have a large lattice mismatch, intermediate phases with different lattice parameters could be generated in the domain walls. In particular, if an orthorhombic structure with smaller lattice parameters is formed in the domain walls, a virtual high-pressure effect is realized on the orthorhombic phase. This constant volume scenario also suggests that the volume ratio in the phase separation region and the pressure range of superconductivity can be different if pressure media with different melting temperatures are used. It is also possible that superconductivity is caused by a uniaxial component of the pressure. Uniaxial stress can also cause a constant volume situation, since the uniaxial pressure is not dynamically maintained through the transition temperature either. Therefore, it may be hard to distinguish this from the constant volume scenario.

The constant volume scenario does not conflict with the diamagnetic signal from high-pressure ac susceptibility on CaFe_2As_2 [12]. If superconductivity is generated in the domain walls to form a thick wall honeycomb-like superconductor, it will be hard to distinguish from bulk superconductivity by transport or susceptibility measurements.

In summary, we have studied the high-pressure susceptibility and the transport properties of CaFe_2As_2 , using helium as the pressure medium. Our data have identified two first order phase transitions separated at

$P \approx 0.35$ GPa. In contrast to other high-pressure studies using clamp cells, we did not see any superconductivity. Therefore, our data indicate that the phase separation and superconductivity in the previous studies are most likely caused by a non-hydrostatic component of pressure. Our results invite caution with respect to the nature of high-pressure superconductivity in all three parent compounds, CaFe_2As_2 , SrFe_2As_2 , and BaFe_2As_2 . We note the proposed third phase under pressure [12] is not seen in our work. Further study is necessary to identify the actual phase properties of the superconducting region. Local probes, such as NMR or μSR , should be useful to perform the studies under non-hydrostatic conditions and verify our scenario.

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